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EXPERIMENTAL EVIDENCE FOR THE 2s STATE
OF THE $\Gamma_{3/2}$ EXCITON IN KI

W. C. Walker*

Physics Department, University of California,
Santa Barbara, California

Recent interpretations of single¹ and double² photon absorption in alkali halides have renewed interest in the higher excited states of excitons in these materials. The experimental evidence for exciton states with $n > 1$ in alkali halides appears to rest mainly with the low temperature (14°K) thin film absorption studies of Fischer and Hilsch in 1959.³ Fine structure attributed by these investigators to higher exciton states apparently was not observed in the similar study of Eby, Teegarden and Dutton.⁴

Structure similar to that of Fischer and Hilsch has recently been observed in the low temperature reflection and luminescent excitation spectrum of KI. A typical excitation spectrum of KI at 80°K taken with 3 angstrom resolution (0.01 eV energy resolution) is shown in Fig. 1. The corresponding near normal incidence reflection spectrum is shown in Figure 2. Luminescent measurements were obtained on a cleaved surface of a Semi-element single crystal held in an oil free vacuum of 2×10^{-7} torr. A photomultiplier having peak response near 4000 Å monitored both the luminescence from the

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KI and that from a sodium salicylate reference screen. The relative luminescent response was taken as the ratio of the two signals. The reflection (10° angle of incidence) spectrum was measured in a vacuum reflectometer on a cleaved surface held in a vacuum of 10^{-9} torr during the measurements.

As has been reported previously,⁵ ultraviolet excited low temperature luminescence in alkali halides has two characteristic features: (a) it appears strongly (quantum yields between 0.1 and 1.0) only in crystals free from significant pre-fundamental impurity absorption bands and (b) the excitation spectrum exhibits the features of the absorption spectrum in an inverse relation; i.e., maxima in absorption correspond to minima in excitation. This latter property leads one to expect to observe absorption fine structure in the excitation spectrum. Comparison of the spectrum of Fig. 1 to the absorption spectrum⁴ interpreted by Phillips⁶ shows that indeed each absorption feature corresponds to an excitation feature to within experimental resolution. This correspondence is indicated in Figure 1 by using the labelling of reference 6 for corresponding features. An extension of the data to 9eV shows the additional structure reported in reference 4 in detail. Because of the precise alignment of excitation and absorption structure it seems likely that the variation in non-radiative surface recombination of the exciton states due to the spectral dependence of the radiation penetration depth is responsible for the correspondence.

The luminescent emission spectrum excited by 7.7 eV radiation was found to consist of a single band centered at 3750 \AA (3.3 eV) with a total width of 1.1 eV. This result is in agreement with that of Teegarden and Weeks⁵ for luminescence excited by 6.1 eV photons. A similar luminescence excited by 50 kilovolt x-rays in KI at 4°K has recently been shown to be due to radiative recombination of trapped holes, i.e. V_k centers, and electrons.⁷ In this case however a double band with centers at 3.33 and 4.0 eV is observed. Such double bands have not yet been seen under ultraviolet excitation. Indeed the existence of the double bands may require free electrons in the conduction band as proposed for the V_k center - free electron recombination process. For this process to occur at excitation energies less than the first direct interband transition an extremely efficient exciton dissociation process would be required. It is possible that the alternate but closely related luminescent process of radiative recombination of the self-trapped exciton dominates for excitation energies between the luminescent onset and the first direct interband transition. The asymmetry in intensity of the excitation spectrum on either side of the 5.81 eV minimum argues in favor of such a description.

The well defined minima in Figure 1 and maxima in Figure 2 at 5.81 and 6.13 eV are of particular interest. Both features are quite reproducible on a variety of samples of "pure" KI. The position, half-width and relative magnitudes of these minima all argue in favor of associating them with the 1s and 2s states of the $\Gamma_{3/2}$ exciton formed from the $\Gamma_{15}^{3/2}$ valence and Γ_1 conduction

bands. Both features have half widths at 80°K of 0.03 to 0.04 eV. The ratio of oscillator strengths as measured roughly by the depths of the minima or height of the maxima is 1:6; a simple hydrogenic n^{-3} dependence would predict a ratio of 1:8. Values of 5.87 and 6.21 eV respectively were obtained by Fischer and Hilsch for these same two states from thin film absorption at 14°K.

Fitting the above two states to a simple hydrogenic model of the form

$$E_{3/2n} = E_{3/2\infty} - 13.605 \frac{\mu}{m \epsilon_0} \frac{1}{n^2} \text{ eV,}$$

where μ is the reduced mass and ϵ_0 the low frequency electronic dielectric constant, taken for KI to be 2.75; gives

$$E_{3/2\infty} = 6.26 \text{ eV, } \mu/m \epsilon_0^2 = 0.45 \text{ eV and } \mu/m = 0.25.$$

These values are nearly identical to those of Fischer and Hilsch if a temperature shift of the order of $10^{-3} \text{ eV/}^\circ\text{K}$ is included. A careful review of the excitation spectrum near the series limit reveals evidence for a weak shoulder at 6.26 eV, corresponding to the $\Gamma_{15}^{3/2} \rightarrow \Gamma_1$ direct absorption edge. Phillips² has placed this edge at 6.1 eV at 80°K on the basis of the data of reference 4. Due to the sparsity of data points between 6.00 and 6.30 eV in the data of ref. 4, the true edge could well occur 0.16 eV higher as determined here.

Although there is some evidence of weak structure in the excitation spectrum which might represent exciton states with $n > 2$, both the resolution and reproducibility of the present data are insufficient to make a positive identification at this time.

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Figure 1. Luminescent excitation spectrum of "pure" KI at 80°K.
The ordinate represents the ratio of the luminescent
yield of KI to that of sodium salicylate.

Figure 2. Reflection spectrum of KI at 80°K.



